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(54) Title: AMINE ORGANOBORANE COMPLEX POLYMERIZATION INITIATORS AND POLYMERIZABLE COMPOSITIONS

(57) Abstract: The invention is an amine-organoborane complex wherein the organoborane is a trialkyl borane and the amine is an amine having an amidine structural component; an aliphatic heterocycle having at least one nitrogen in the heterocyclic ring wherein the heterocyclic compound may also contain one or more nitrogen atoms, oxygen atoms, sulfur atoms, or double bonds in the heterocycle; a primary amine which in addition has one or more hydrogen bond accepting group wherein there is at least two carbon atoms, preferably three, between the primary amine and the hydrogen bond accepting group, such that due to inter- or intramolecular interactions within the complex the strength of the B-N bond is increased; or a conjugated imine. Preferred hydrogen bond accepting groups include the following: a secondary amine, a tertiary amine, an ether, a halogen, a polyether group or a polyamine group. The complexes of the invention are used in polymerizable compositions, adhesive compositions and coatings compositions containing compounds having moieties which polymerise under free radical polymerization conditions.

AMINE ORGANOBORANE COMPLEX POLYMERIZATION INITIATORS AND POLYMERIZABLE COMPOSITIONS

This invention relates to organoborane amine complexes that are useful as free radical polymerization initiators. In another embodiment, this invention relates to polymerizable compositions comprising compounds containing moieties capable of free radical polymerization and organoborane amine complex initiators of the invention. In yet another embodiment the invention relates to adhesive, sealant, coating and ink compositions containing organoborane amine complexes and compounds containing moieties capable of free radical polymerization.

In many practical situations in which compounds are subjected to polymerization or where adhesives are used, it is desirable to have polymerizable compositions and adhesive compositions which can cure on demand. Cure on demand means that the polymerization can be initiated when desired. A significant problem with cure on demand compositions is the stability of the compositions. Many such compositions will begin curing at, or near, ambient temperature or will partially cure at ambient temperature resulting in an increased viscosity causing difficulties in handling and reduced functionality of the polymerizable composition or adhesive composition.

Low surface energy olefins such as polyethylene, polypropylene and polytetrafluroethylene have a variety of attractive properties in a variety of uses, such as for toys, automobile parts and furniture applications. Because of the low surface energy of these plastic materials, it is very difficult to find adhesive compositions which bond to these materials. The commercially available adhesives which are used for these plastics require time consuming or extensive pretreatment of the surface before the adhesive will bond to the surface. Such pretreatments include corona treatment and flame treatment. The requirement for extensive pretreatment of the surface results in significant limitations to the designers of automobile components, toys and furniture. What is needed is adhesive compositions which are capable of bonding to low surface energy substrates, and bonding

low surface energy substrates to other substrates, without the need for extensive or costly pretreatment.

Mottus et al., US Patent 3,275,611 discloses a process for polymerizing olefinic compounds with a catalyst comprising an organoborane compound, a peroxygen compound and an amine. It is disclosed that the organoborane compound and amine may be added to the reaction mixture separately or as a preformed complex, and that the complex is preferred. The presence of the amine in the complex reduces the pyrophoricity of the organoborane in air. Among the amine complexing agents disclosed are pyridine, aniline, toluidine, dimethylbenzylamine, and nicotine. Many of the complexes disclosed in Mottus are pyrophoric at all amine to boron atom ratios. In addition, many of the amine complexes do not display significant adhesive properties when applied to low surface energy substrates.

A series of patents issued to Skoultchi (US Patent Nos. 5,106,928, 5,143,884, 5,286,821, 5,310,835 and 5,376,746) disclose a two-part initiator system that is reportedly useful in acrylic adhesive compositions. The first part of the two-part system includes a stable organoborane-amine complex and the second part includes a destabilizer or activator such as an organic acid or an aldehyde. The organoborane compound of the complex has three ligands which can be selected from C_{1-10} alkyl groups or phenyl groups. Useful amines disclosed include octylamine, 1,6 diaminohexane, diethylamine, dibutylamine, diethylenetriamine, dipropylenediamine, 1,3 propylene diamine, and 1,2 propylene diamine. The adhesive compositions are disclosed to be useful in structural and semi-structural adhesive applications, such as speaker magnets, metal to metal bonding, automotive glass to metal bonding, glass to glass bonding, circuit board component bonding, bonding select plastics to metal, glass to wood, etc. and for electric motor magnets.

Zharov et al. discloses in a series of US Patents (US 5,539,070; US 5,690,780; and US 5,691,065) polymerizable acrylic compositions which are particularly useful as adhesives wherein organoborane amine complexes are used to initiate cure. The organoboranes used have three ligands attached to the borane atom which are selected from C_{1-10} alkyl groups and phenyl. The amine is an alkanol amine or a diamine where the first amine group can be a primary or secondary amine and the second amine is a primary amine.

It is disclosed that these complexes are good for initiating polymerization of an adhesive which bonds to low surface energy substrates.

Pocius in a series of patents (US 5,616,796; US 5,6211,43; US 5,681,910; US 5,686,544; US 5,718,977; and US 5,795,657) disclose amine organoborane complexes with a variety of amines such as polyoxyalkylene polyamines and polyamines which are the reaction product of diprimary amines and compound having at least two groups which react with a primary amine.

Many of the complexes disclosed in the Zharov, Skoultchi and Pocius Patents are not stable in compositions containing olefinic unsaturation at, or near, ambient temperatures and thus the complexes disassociate and induce polymerization at, or near, ambient temperature with time. This instability at, or near, ambient temperature can result in polymerization before desired and can result in compositions which are unsuitable for the desired use.

Therefore, there is a need for initiator systems for free radical polymerization which are safe to handle, not pyrophoric, which can be used to form cure on demand polymer systems or can be used in adhesive systems which cure on demand. What is further needed are adhesive systems which are capable of bonding to low surface energy substrates, and initiator systems which facilitate such bonding. In addition to such needs, the complexes need to be thermally stable, that is do not disassociate at, or near, ambient temperatures and thereby initiate polymerization before desired. What are further needed are polymer compositions and adhesive systems which are thermally stable at, or near, ambient temperatures and which will undergo polymerization when the user desires.

In one embodiment the invention is an amine organoborane complex wherein the organoborane is a trialkyl borane and the amine is selected from the group of amines having an amidine structural component; aliphatic heterocycles having at least one nitrogen in the heterocyclic ring wherein the heterocyclic compound may also contain one or more nitrogen atoms, oxygen atoms, sulfur atoms, or double bonds in the heterocycle; primary amines which in addition have one or more hydrogen bond accepting groups wherein there are at least two carbon atoms, preferably at least three carbon atoms, between the primary amine and the hydrogen bond accepting group, such that due to inter- or intramolecular

interactions within the complex the strength of the B-N bond is increased; and conjugated imines. Preferred hydrogen bond accepting groups include the following: primary amines, secondary amines, tertiary amines, ethers, halogens, polyethers or polyamines. Heterocycle as used herein refers to a compound having one or more aliphatic cyclic rings of which one of the rings contains nitrogen. The amidines or conjugated imines can be straight or branched chain or cyclic.

In another embodiment the invention comprises a polymerizable composition which comprises an amine organoborane complex of the invention and one or more of monomers, oligomers or polymers having olefinic unsaturation which are capable of polymerization by free radical polymerization. This composition can undergo polymerization by exposing the composition to temperatures at which the organoborane amine complex undergoes disassociation. In another embodiment the invention is a polymerizable composition which further comprises an effective amount of a compound which causes the complex to disassociate (decomplexing agent), thereby freeing the borane to initiate polymerization of the one or more monomers, oligomers or polymers having olefinic unsaturation. The compound which causes disassociation of the complex is kept separate from the complex until initiation of polymerization is desired. In yet another embodiment the invention is a method of polymerization comprising a contacting of the components of the polymerizable compositions under conditions that the one or more monomers, oligomers or polymers undergo polymerization. The polymerizable composition which contains the decomplexing agent can be cured at any desired temperature, such as at, or near, ambient temperature and below ambient temperature.

The polymerizable compositions of the invention can be used as adhesive, sealant, coating or ink compositions. In one embodiment two or more substrates are bonded together by contacting the components of the adhesive composition of the invention, including the decomplexing agent, together under conditions such that polymerization is initiated; contacting the adhesive composition with the two or more substrates; positioning the two or more substrates such that the adhesive composition is located between the two or more substrates wherein they are in contact with one another; and allowing the adhesive to cure so as to bond the two or more substrates together. The thermally curing compositions of the invention can be used to bond two or more substrates together by contacting the

adhesive composition with the substrates such that the adhesive composition is located between the two or more substrates and exposing the adhesive composition to a temperature at which the complex disassociates and initiating the free radical polymerization of the monomer, oligomers, polymers or a mixture thereof.

The complexes of the invention are safe to handle, not pyrophoric, are stable at, or near, ambient temperature and therefore will not initiate polymerization at, or near, ambient temperature in the absence of an initiator that causes the complex to disassociate. The polymeric compositions of the invention are stable at, or near, ambient temperature and can be cured upon demand by contacting the complex with the compounds which cause disassociation of the complex, or alternatively by heating the polymeric compositions above the thermal disassociation temperature of the complex. Furthermore, the adhesive, sealant, coating and ink compositions of the invention can form good bonds to low surface energy substrates without the need for primers or surface treatment.

The organoborane used in the complex is a trialkyl borane or an alkyl cycloalkyl borane. Preferably such borane corresponds to Formula 1:

$$B \leftarrow (R^2)_3 \qquad \text{Formula 1}$$

wherein B represents Boron; and R^2 is separately in each occurrence a C_{1-10} alkyl, C_{3-10} cycloalkyl , or two or more of R^2 may combine to form a cycloaliphatic ring. Preferably R^2 is C_{1-4} alkyl, even more preferably C_{2-4} alkyl, and most preferably C_{3-4} alkyl. Among preferred organoboranes are tri-ethyl borane, tri-isopropyl borane and tri-n-butylborane. To prepare thermally stable polymerizable compositions, thermally stable complexes which do not disassociate, at or near, ambient temperature are needed. The key to preparation of such complexes, is the selection of the amine. The desirability of the use of a given amine in an amine/organoborane complex can be calculated from the energy difference between the Lewis acid-base complex and the sum of energies of the isolated Lewis acid (organoborane) and base (amine) known as binding energy. The higher the binding energy the more stable the complex.

Binding Energy =

-(Complex Energy - (Energy of Lewis Acid + Energy of Lewis base))

Such binding energies can be calculated using theoretical *ab-initio* methods such as the Hartree Fock method and the 3-21G basis set. These computational methods are available commercially employing commercial software and hardware such as SPARTAN and GAUSSIAN 98 programs with a Silicon Graphics workstation. Amines having amine/organoborane binding energies of ten kilocalories per mol or greater are preferred, amines having a binding energy of 15 kilocalories per mol or greater are more preferred and even more preferred are amines with a binding 20 kilocalories per mol or greater. In the embodiment where polymerization of the compositions of the invention is initiated by use of a decomplexing agent the binding energy of the amine to the organoborane is preferably about 50 kcal/mole or less and most preferably about 30 kcal/mole or less. In the embodiment where polymerization of the compositions of the invention is initiated by use of heat the binding energy of the amine is preferably about 100 kcal/mole or less, more preferably about 80 kcal/mole or less and most preferably about 50 kcal/mole or less.

In one embodiment, the amine comprises a compound having a primary amine and one or more hydrogen bond accepting groups, wherein there are at least two carbon atoms, preferably at least about three, between the primary amine and hydrogen bond accepting groups. Hydrogen bond accepting group means herein a functional group that through either inter- or intramolecular interaction with a hydrogen of the borane-complexing amine increases the electron density of the nitrogen of the amine group complexing with the borane. Preferred hydrogen bond accepting groups include primary amines, secondary amines, tertiary amines, ethers, halogen, polyethers, and polyamines. In a preferred embodiment, the amine corresponds to Formula 2:

$$NH_2\left(CH_2\right)_b\left(C\left(R^1\right)_2\right)_a X \qquad \text{Formula 2}$$

wherein:

R^1 is separately in each occurrence hydrogen or a C_{1-10} alkyl or C_{3-10} cycloalkyl;

X is hydrogen bond accepting moiety; a is an integer of 1 to 10; and b is separately in each

occurrence an integer of 0 to 1, and the sum of a and b is from 2 to 10. Preferably R^1 is hydrogen or methyl. Preferably X is separately in each occurrence a hydrogen accepting moiety with the proviso that when the hydrogen accepting, moiety is an amine it is a tertiary or a secondary amine. More preferably X is separately in each occurrence $-N(R^8)_e$, $-OR^{10}$, or a halogen wherein R^8 is separately in each occurrence C_{1-10} alkyl, C_{3-10} cycloalkyl or $-(C(R^1)_2)_d-W$; R^{10} is separately in each occurrence, C_{1-10} alkyl, C_{3-10} cycloalkyl, or $-(C(R^1)_2)_d-W$; and e is 0, 1, or 2. More preferably X is $-N(R^8)_2$ or $-OR^{10}$. Preferably, R^8 and R^{10} are C_{1-4} alkyl or $-(C(R^1)_2)_d-W$, more preferably C_{1-4} alkyl and most preferably methyl. W is separately in each occurrence hydrogen or C_{1-10} alkyl or X and more preferably hydrogen or C_{1-4} alkyl. Preferably, a is about 1 or greater and more preferably 2 or greater. Preferably a is about 6 or less, and most preferably about 4 or less. Preferably, b is about 1. Preferably, the sum of a and b is an integer about 2 or greater and most preferably about 3 or greater. Preferably the sum of a and b are about 6 or less and more preferably about 4 or less. Preferably d is separately in each occurrence an integer of 1 to 4, more preferably 2 to 4, and most preferably 2 to 3. Among preferred amines corresponding to Formula 2 are dimethylaminopropyl amine, methoxypropyl amine, dimethylaminoethylamine, dimethylaminobutylamine, methoxybutyl amine, methoxyethyl amine, ethoxypropylamine, propoxypropylamine, amine terminated polyalkylene ethers (such as trimethylolpropane tris(poly(propyleneglycol), amine terminated)ether), aminopropylmorpholine, isophoronediamine, and aminopropylpropanediamine.

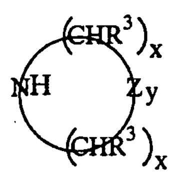
In one embodiment the preferred amine complex corresponds to Formula 3:

$$(R^2)_3 B \longleftarrow NH_2(CH_2)_b(C(R^1)_2)_a$$

Formula 3

wherein R^1, R^2, X, a and b are as defined hereinbefore.

In another embodiment the amine is an aliphatic heterocycle having at least one nitrogen in the heterocycle. The heterocyclic compound may also contain one or more of nitrogen, oxygen, sulfur or double bonds. In addition, the heterocycle may comprise multiple rings wherein at least one of the rings has a nitrogen in the ring. Preferably the aliphatic heterocylic amine corresponds to Formula 4:



Formula 4

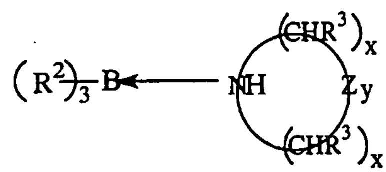
wherein:

R^3 is separately in each occurrence hydrogen, a C_{1-10} alkyl or C_{3-10} cycloalkyl;

Z is separately in each occurrence oxygen or NR^4 wherein R^4 is hydrogen, C_{1-10} alkyl, or C_{6-10} aryl or alkaryl;

x is separately in each occurrence an integer of 1 to 10, with the proviso that the total of all occurrences of x should be from 2 to 10; and y is separately in each occurrence 0 or 1. Preferably, R^3 is separately in each occurrence hydrogen or methyl. Preferably Z is NR^4. Preferably, R^4 is hydrogen or C_{1-4} alkyl, and more preferably hydrogen or methyl. Preferably x is from 1 to 5 and the total of all the occurrences of x is 3 to 5. Preferred compounds corresponding to Formula 4 include morpholine, piperidine, pyrolidine, piperazine, 1,3,3 trimethyl 6-azabicyclo[3,2,1] octane, thiazolidine, homopiperazine, aziridine, 1,4-diazabicylo[2.2.2]octane (DABCO), 1-amino-4-methylpiperazine, and 3-

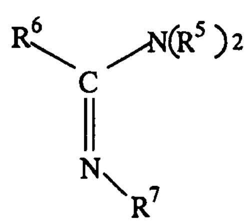
pyrroline. Complexes using aliphatic heterocyclic amines preferably correspond to Formula 5:



Formula 5

wherein R^2, R^3, Z, x and y are as defined hereinbefore.

In yet another embodiment, the amine which is complexed with the organoborane is an amidine. Any compound with amidine structure wherein the amidine has sufficient binding energy as described hereinbefore with the organoborane, may be used. Preferable amidine compounds correspond to Formula 6:

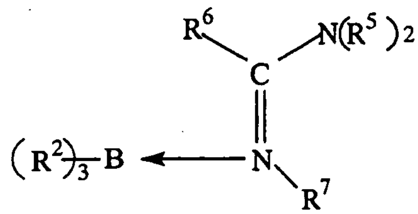


Formula 6

wherein:

R^5, R^6, and R^7 are separately in each occurrence hydrogen, a C_{1-10} alkyl or C_{3-10} cycloalkyl; two or more of R^5, R^6, and R^7 may combine in any combination to form a ring structure, which may have one or more rings. Preferably R^5, R^6 and R^7 are separately in each occurrence hydrogen, C_{1-4} alkyl or C_{5-6} cycloalkyl. Most preferably R^7 is H or methyl. In the embodiment where two or more of R^5, R^6 and R^7 combine to form a ring structure the ring structure is preferably a single or a double ring structure. Among preferred amidines are 1,8 diazabicyclo[5,4]undec-7-ene; tetrahydropyrimidine; 2-methyl-2-imidazoline; and 1,1,3,3-tetramethylguanidine.

The organoborane amidine complexes preferably correspond to Formula 7:



Formula 7

wherein R^2, R^5, R^6 and R^7 are as defined earlier.

In yet another embodiment, the amine which is complexed with the organoborane is a conjugated imine. Any compound with a conjugated imine structure, wherein the imine has sufficient binding energy as described hereinbefore with the organoborane, may be used. The conjugated imine can be a straight or branched chain imine or a cylic imine. Preferable imine compounds correspond to Formula 8:

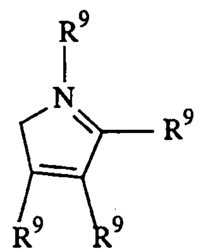
$$NR^7{=}CR^9\text{—}(CR^9{=}CR^9)_c \qquad \text{Formula 8}$$

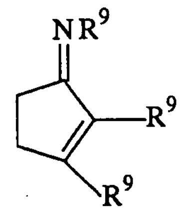
wherein Y is independently in each occurrence hydrogen, $N(R^4)_2$, OR^4, $C(O)OR^4$, halogen or an alkylene group which forms a cyclic ring with an R^7 or R^9. R^4 is hydrogen, C_{1-10} alkyl, or C_{6-10} aryl or alkaryl. Preferably R^4 is hydrogen or methyl. R^7 is as described previously. R^9 is independently in each occurrence hydrogen, Y, C_{1-10} alkyl, C_{3-10} cycloalkyl–, $(C(R^9)_2$-$(CR^9{=}CR^9)_c$-Y or two or more of R^9 can combine to form a ring structure provided the ring structure is conjugated with respect to the double bond of the imine nitrogen; and c is an integer of from 1 to 10. Preferably, R^9 is hydrogen or methyl.

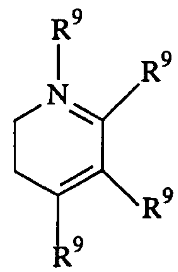
Y is preferably $N(R^4)_2$, or OR^4, or an alkylene group which forms a cyclic ring with R^7 or R^9. Y is more preferably $N(R^4)_2$ or an alkylene group which forms a cyclic ring with R^7 or R^9. Preferably, c is an integer of from 1 to 5, and most preferably about 1. Among preferred

conjugated imines useful in this invention are 4-dimethylaminopyridine; 2,3-bis(dimethylamino)cyclopropeneimine; 3-(dimethylamine)acroleinimine; 3-(dimethylamino)methacroleinimine.

Among preferred cyclic imines are those corresponding to the following structures







The complexes with the conjugated imines preferably correspond to Formula 9:

$$(R^2)_3B \leftarrow NR^7{=}CR^9{-}(CR^9{=}CR^9)_c \qquad \text{Formula 9}$$

wherein R^2, R^7,R^9, c and Y are as defined hereinbefore.

The molar ratio of amine compound to borane compound in the complex is relatively important. In some complexes if the molar ratio of amine compound to organoborane compound is too low, the complex is pyrophoric. Preferably the molar ratio of amine compound to organoborane compound is from 1.0:1.0 to 3.0:1.0. Below the ratio of about 1.0:1.0 there may be problems with polymerization, stability of the complex and for adhesive uses, adhesion. Greater than about a 3.0:1.0 ratio may be used although there is no

benefit from using a ratio greater than about 3.0:1.0. If too much amine is present, this may negatively impact the stability of the adhesive or polymer compositions. Preferably the molar ratio of amine compound to organoborane compound is from 2.0:1.0 to 1.0:1.0.

Polymerizable compounds which may be used in the polymerization compositions of the invention include any monomers, oligomers, polymers or mixtures thereof which contain olefinic unsaturation which can polymerize by free radical polymerization. Such compounds are well known to those skilled in the art. Mottus, US Patent Number 3,275,611, provides a description of such compounds at column 2, line 46 to column 4, line 16, incorporated herein by reference. Among preferred classes of compounds containing olefinic unsaturation are monomers, oligomers, polymers and mixtures thereof derived from the acrylates and methacrylates; olefinically unsaturated hydrocarbons, for example ethylene, propylene, butylene, isobutylene, 1-octene, 1-dodecene, 1-heptadecene, 1-eicosene; vinyl compounds such as styrene, vinyl pyridine, 5-methyl-2 vinylpyridine, vinyl napthylene, alpha methylstyrene; vinyl and vinylidiene halides; acrylonitrile and methacrylonitrile; vinyl acetate and vinyl propionate; vinyl oxyethanol; vinyl trimethylacetate; vinyl hexonate; vinyl laurate; vinyl chloroacetate; vinyl stearate; methyl vinyl ketone; vinyl isobutyl ether; vinyl ethyl ether; compounds that have a plurality of ethylenic bonds such as those having conjugated double bonds such as butadiene, 2 chlorobutadiene, isoprene. Examples of preferable acrylates and methacrylates are disclosed in Skoultchi, US Patent Number 5,286,821 at column 3, lines 50 to column 6, line 12, incorporated herein by reference and Pocius, US Patent Number 5,681,910 at column 9, line 28 to column 12, line 25, incorporated herein by reference. More preferred olefinic compounds comprise methyl acrylate, methylmethacrylate, butylmethacrylate, tert-butylmethacrylate, 2-ethylhexyacrylate, 2-ethylhexylmethacrylate, ethylacrylate, isobornylmethacrylate, isobornylacrylate, hydroxyethylmethacrylate, glycidylmethacrylate, tetrahydrofurfuryl methacrylate, acrylamide, n-methylacrylamide, and other similar acrylate containing monomers. Also useful are the class of acrylate tipped polyurethane prepolymers available commercially from several sources, and prepared by reacting an isocyanate reactive acrylate monomer, oligomer or polymer, such as a hydroxy acrylate, with an isocyanate functional prepolymer.

In the embodiment where the composition is used as an adhesive, acrylate and/or methacrylate based compounds are preferably used. The most preferred acrylate and methacrylate compounds include methylmethacrylate, butylmethacrylate, 2-ethylhexylmethacrylate, isobornylmethacrylate, tetrahydrofurfuryl methacrylate, and cyclohexylmethylmethacrylate.

In some embodiments the polymerizable compositions of the invention may further comprise an effective amount of a compound that is reactive with an amine so as to liberate the organoborane so as to initiate polymerization (a decomplexing agent). The amine reactive compound liberates organoborane by reacting with the amine, thereby removing the organoborane from chemical attachment with the amine. Desirable amine reactive compounds are those materials that can readily form reaction products with amines at or below and more preferably at room temperature about 20°C to 22°C so as to provide a composition that can be generally easily used and cured under ambient conditions. General classes of such compounds include acids, aldehydes, isocyanates, acid chlorides, sulphonyl chlorides, mixtures thereof. Preferred amine reactive compounds are acids. Both Bronstead and Lewis acids may be used. Pocius, US Patent Number 5,718,977 describes the preferred acid compounds at column 9, line 1 to 15 incorporated herein by reference. The most preferred acids are acrylic acid and methacrylic acid.

Preferably the amount of polymerizable compounds in the polymerizable compositions or adhesive is about 20 percent by weight or greater based on the weight of the total composition, more preferably about 30 percent by weight or greater and most preferably about 40 percent by weight or greater. Preferably the amount of polymerizable compounds is about 95 percent by weight or less, preferably about 90 percent by weight or less and most preferably about 85 percent by weight or less. The amount of complex used in the composition can be any amount sufficient to initiate polymerization once the complex has disassociated at the desired speed of polymerization. At higher concentration of organoborane, the speed of polymerization is higher. Preferably the amount of organoborane complex is about 0.2 percent by weight or greater based on the weight of the total composition, preferably about 1.0 percent by weight or greater and most preferably about 2 percent by weight or greater. Preferably the amount of organoborane complex present is about 8 percent by weight or less based on the total weight of composition, preferably about

6 percent by weight or less and most preferably about 4 percent by weight or less. In those embodiments where a decomplexing agent is used, the amount of decomplexing agent (initiator) is that amount which is sufficient to initiate disassociation of the organoborane-amine complex thereby causing the organoborane to initiate polymerization of the olefinically unsaturated compound. Preferably the amount of decomplexing agent is about 1 percent by weight or greater based on the weight of the total composition, more preferably about 1.5 percent by weight or greater and most preferably about 2 percent by weight or greater. Preferably the amount of decomplexing agent is about 8 percent by weight or less based on the weight of the total composition, more preferably about 6 percent by weight or less and most preferably about 4 percent by weight or less.

The organoborane amine complex may be readily prepared using known techniques. Typically, the amine is combined with the organoborane in an inert atmosphere with slow stirring. An exotherm is often observed and cooling of the mixture is, therefore, recommended. If the ingredients have a high vapor pressure, it is desirable to keep the reaction temperature below about 70°C to 80°C. Once the materials are well mixed the complex is permitted to cool to room temperature. No special storage conditions are required although it is preferred that the complex be kept in a capped vessel under an inert atmosphere, in a cool, dark location. Advantageously, the complexes of the invention can be prepared in the absence of organic solvents that would later have to be removed, although they could be prepared in solvent, if so desired. Solvents used in the preparation of the complexes should, preferably, be ones that do not coordinate the amine, preferable solvents are for example, tetrahydrofuran or diethylether, or low molecular weight alkanes such as hexane or heptane.

The invention are air stable. By "air stable" it is meant that when the complexes are stored in a capped vessel at room temperature (about 20°C to 22°C) and under otherwise ambient conditions (that is, not under a vacuum and not in an inert atmosphere), the complexes remain useful as polymerization initiators for at least about two weeks, although the complexes may be readily stored under these conditions for many months.

By "air stable" it is also meant that the complexes are not pyrophoric. (When a few drops of the complex are placed on a paper towel under ambient conditions, the paper towel does not ignite, char or smoke.) The air stability of the complex is enhanced when the complex is a crystalline material. However, the complexes of the invention are air stable for at least six months even when they are liquids. Liquid complexes are easier to handle and mix than are crystalline complexes.

The polymerizable compositions of the invention can be either one or two-part compositions depending upon the mechanism used to initiate polymerizations. In one embodiment the compositions are two-part compositions in which one-part contains the complexes of the invention and the other part contains the decomplexing agent (initiator). Polymerization is initiated by contacting the two-parts of the composition. An advantage of this process is that polymerization can be initiated at, or even below, ambient temperatures. In this embodiment heat may be applied to the polymerizable composition to speed up initiation or polymerization. In another embodiment the polymerization composition may be initiated by heating the composition. In this embodiment no decomplexing agent (initiator) is needed. When polymerization is initiated by heating the composition can be either a one-part or a two-part composition. The primary reason to use a two-part composition is to keep apart components of the composition which may be unstable in the presence of one another. Generally a one-part composition is preferred in this embodiment as the delivery equipment is less complex and costly and the need to properly ratio the components is eliminated.

In the embodiment where heat is used to initiate the cure of the composition, the composition is exposed to a heat source which heats the composition to a temperature at or above the temperature at which the complex used in the composition decomposes to release the organoborane which then initiates free radical polymerization. Generally the composition is heated to a temperature which is less than the temperature at which the polymer formed undergoes degradation. The temperature at which the complex undergoes disassociation is related to the binding energy of the complex. At higher binding energies of the complex higher temperatures are required to initiate polymerization. In the embodiment where the polymerization is initiated thermally the temperature at which the composition is heated to initiate polymerization is dictated by the binding energy of the complex.

Generally the temperature used to initiate the polymerization by decomplexing the complex is about 30°C or greater and preferably about 50°C or greater. Preferably the temperature at which thermally initiated polymerization is initiated is about 120°C or less and more preferably about 100°C or less. Any heat source which heats the composition to the desired temperature can be used provided the heat source does not negatively impact the components of the composition or its function. In this manner the composition may be contacted with the substrates either before or after the composition is exposed to heat. If the composition is heated prior to contact with the substrates, the composition should be contacted with the substrates before the composition has polymerized to the point at which the composition is no longer able to adhere to the substrates, this is usually the upper limit on the open time as defined hereinafter. It may be necessary in the thermally initiated reaction to control the oxygen content such that there is adequate oxygen to create favorable conditions for radical formation but not so much as to inhibit the polymerization.

The two-part polymerizable compositions or adhesive compositions of the invention are uniquely suited for use with conventional, commercially available dispensing equipment for two-part adhesives. Once the two-parts have been combined, the composition should be used quickly, as the useful pot life (or open time) may be short depending upon the monomer mix, the amount of complex, and the temperature at which the bonding is to be performed. The adhesive composition is applied to one or both substrates and then the substrates are joined together with pressure to force excess composition out of the bond line. This also has the advantage of displacing composition that has been exposed to air and that may have begun to react. In general, the bonds should be made shortly after the composition has been applied, preferably within about 10 minutes. The typical bond line thickness is about 0.005 inches (0.13 mm) to about 0.03 inches (0.76 mm). The bonding process can easily be carried out at room temperature and to improve the degree of polymerization it is desirable to keep the temperature below about 40°C, preferably below about 30°C, and most preferably below about 25°C.

The bonds will cure to a reasonable green strength to permit handling of the bonded components within about 2 to 3 hours. Full strength will be reached in about 24 hours under ambient conditions; post-curing with heat (typically about 80°C) may be used if desired.

When bonding fluoroplastics, it is advantageous to cool the initiator containing part of the two-part composition to 0°C to 5°C before adding the organoborane amine complex. The bond should be made as soon after the composition has been applied as practical; performing the bonding operation at less than about room temperature is also helpful.

The compositions may further comprise a variety of optional additives. One particularly useful additive is a thickener such as medium to high (10,000 to 1,000,000) molecular weight polymethyl methacrylate which may be incorporated in an amount of 10 to 60 weight percent, based on the total weight of the composition. Thickeners may be employed to increase the viscosity of the composition to facilitate application of the composition.

Another particularly useful additive is an elastomeric material. The materials can improve the fracture toughness of compositions made therewith which can be beneficial when, for example, bonding stiff, high yield strength materials such as metal substrates that do not mechanically absorb energy as easily as other materials, such as flexible polymeric substrates. Such additives can be incorporated in an amount of 5 percent to 35 percent by weight, based on the total weight of the composition. Useful elastomeric modifiers include chlorinated or chlorosulphonated polyethylenes such as HYPALON 30 (commercially available from E. I. Dupont de Nemours & Co., Wilmington, Delaware) and block copolymers of styrene and conjugated dienes (commercially available from Dexco Polymers under the Trademark VECTOR, and Firestone under the Trademark STEREON). Also useful, and even more preferred, are certain graft copolymer resins such as particles that comprise rubber or rubber-like cores or networks that are surrounded by relatively hard shells, these materials often being referred to as "core-shell" polymers. Most preferred are the acrylonitrile-butadiene-styrene graft copolymers available from Rohm and Haas. In addition to improving the fracture toughness of the composition, core-shell polymers can also impart enhanced spreading and flow properties to the uncured composition. These enhanced properties may be manifested by a reduced tendency for the composition to leave an undesirable "string" upon dispensing from a syringe-type applicator, or sag or slump after having been applied to a vertical surface. Use of more than about 20 percent of a core-shell polymer additive is desirable for achieving improved sag-slump resistance. Generally

the amount of toughening polymer used is that amount which gives the desired toughness to the polymer or the adhesive prepared.

Another useful adjuvant is a cross-linking agent. Cross-linking agents can be used to enhance the solvent resistance of the adhesive bond or polymer composition, although certain compositions of the invention have good solvent resistance even in the absence of externally added cross-linking agents. Typically employed in an amount of 0.2 to 10 weight percent based on the total weight of the compositions, useful cross-linkers include the various diacrylates referred to above as possible acrylic modifying monomers as well as other materials. Particular examples of suitable cross-linking agents include ethylene glycol dimethacrylate, ethylene glycol diacrylate, triethyleneglycol dimethacrylate, diethylene glycol bismethacryloxy carbonate, polyethylene glycol diacrylate, tetraethylene glycol dimethacrylate, diglycerol diacrylate, diethylene glycol dimethacrylate, pentaerythritol triacrylate, trimethylolpropane triglycidyl ether, trimethylolpropane tris(2-methyl-1-aziridinepropionate, trimethylolpropane trimethacrylate, acrylate tipped polyurethane containing prepolymers, polyether diacrylates and dimethacrylates.

Peroxides may be optionally included (typically in an amount of about 2 percent by weight or less, based on the total weight of the composition), for example, to adjust the speed at which the compositions polymerize or to complete the polymerization.

Small amounts of inhibitors such as hydroquinone may be used, for example, to prevent or reduce degradation of the olefinic monomers during storage. Inhibitors may be added in an amount that does not materially reduce the rate of polymerization or the ultimate properties of an adhesive or other composition made therewith, typically 10 to 10,000 ppm based on the weight of the polymerizable monomers.

Other possible additives include non-reactive colorants, fillers (for example, carbon black), etc.

The various optional additives are employed in an amount that does not significantly adversely affect the polymerization process or the desired properties of compositions made therewith.

Polymerizable compositions according to the invention may be used in wide variety of ways, including as sealants, coatings, primers, to modify the surface of polymers, and injection molding resins. They may also be used as matrix resins in conjunction with glass and metal fiber mats such as in resin transfer molding operations. They may further be used as encapsulants and potting compounds such as in the manufacture of electrical components, printed circuit boards. Quite desirably, they provide polymerizable adhesive compositions that can bond a diverse myriad of substrates, including polymers, wood, ceramics, concrete, glass and primed metals. Another desirable related application is their use in promoting adhesion of paints to low surface energy substrates such as polyethylene, polypropylene, polyethyleneterephthalate and polytetrafluoroethylene, and their co-polymers. In this embodiment the composition is coated onto the surface of the substrate to modify the surface to enhance the adhesion of the final coating to the surface of the substrate.

The compositions of the invention can be used in coating applications. In such applications the composition may further comprise a carrier such as water or a solvent. The coating may further contain additives well known to those skilled in the art for use coatings such as pigments to color the coating, inhibitors and UV stabilizers. The compositions may also be applied as powder coatings and may contain the additives well known to those skilled in the art for use in powder coatings.

The compositions of the invention can also be used to modify the surface of a polymeric molded part, extruded film or contoured object. Compositions of the invention can also be used to change the functionality of a polymer particle by surface grafting of polymer chains on to the unmodified plastic substrate.

Alternatively, the complexes of the present invention can be dissolved in a variety of solvents including water or organic solvents that provide a non acid containing environment and used as a primer. In this manner the complex containing solution is applied to the surface that is to be used for adhesion, surface modification, or polymerization, and the solvent allowed to dry. The polymerizable monomer is then brought into contact with the complex on the surface and allowed to react for the purpose of promoting adhesion, or surface modification, or for initiating radical polymerization.

Polymerizable compositions of the invention are especially useful for adhesively bonding low surface energy plastic or polymeric substrates that historically have been very difficult to bond without using complicated surface preparation techniques, priming, etc. By low surface energy substrates is meant materials that have a surface energy of about 45 mJ/m^2 or less, more preferably about 40 mJ/m^2 or less and most preferably about 35 mJ/m^2 or less. Included among such materials are polyethylene, polypropylene, acrylonitrile-butadiene-styrene, polyamides, syndiotactic polystyrene, olefin containing block co-polymers, and fluorinated polymers such as polytetrafluoroethlene (TEFLON) which has a surface energy of less than about 20 mJ/m^2. (The expression "surface energy" is often used synonymously with "critical wetting tension" by others.) Other polymers of somewhat higher surface energy that may be usefully bonded with the compositions of the invention include polycarbonate, polymethylmethacrylate, and polyvinylchloride.

The polymerizable compositions of the invention can be easily used as two-part adhesive. The components of the polymerizable compositions are blended as would normally be done when working with such materials. The decomplexing agent is usually included in this blend so as to separate it from the organoborane amine complex, thus providing one-part of the two-part composition. The organoborane amine complex of the polymerization initiator system provides the second part of the composition and is added to the first part shortly before it is desired to use the composition. The complex may be added to the first part directly or it may be pre-dissolved in an appropriate carrier such as methyl methacrylate.

It may be desirable to store the complexes apart from the monomers, oligomers or polymers to inhibit premature polymerization of the monomers, oligomers or polymers. The complexes of this invention have greatly enhanced stability when in the presence of monomers and in the absence of a decomplexing agent, such as an acid, and thus can be stored with the polymerizable components of the composition. Complexes in which the complexing amine nitrogen atom to boron atom ratio is greater than 1:1 may be sufficiently stable that they can be blended with polymerizable components in useful proportions. However, in such situations, the presence of additional non-polymerizing reactants (for example, the organoborane liberator) may result in other, undesirable affects.

For a two-part adhesive such as those of the invention to be most easily used in commercial and industrial environments, the ratio at which the two-parts are combined should be a convenient whole number. This facilitates application of the adhesive with conventional, commercially available dispensers. Such dispensers are shown in US Patent Nos. 4,538,920 and 5,082,147 (incorporated herein by reference) and are available from Conprotec, Inc. (Salem New Jersey) under the trade name MIXPAC. Typically, these dispensers use a pair of tubular receptacles arranged side-by-side with each tube being intended to receive one of the two-parts of the adhesive. Two plungers, one for each tube, are simultaneously advanced (for example, manually or by a hand-actuated ratcheting mechanism) to evacuate the contents of the tubes into a common, hollow, elongated mixing chamber that may also contain a static mixer to facilitate blending of the two-parts. The blended adhesive is extruded from the mixing chamber onto a substrate. Once the tubes have been emptied, they can be replaced with fresh tubes and the application process continued.

The ratio at which the two-parts of the adhesive are combined is controlled by the diameter of the tubes. (Each plunger is sized to be received within a tube of fixed diameter, and the plungers are advanced into the tubes at the same speed.) A single dispenser is often intended for use with a variety of different two-part adhesives and the plungers are sized to deliver the two-parts of the adhesive at a convenient mix ratio. Some common mix ratios are 1:1, 2:1, 4:1 and 10:1.

The part of the adhesive or polymerizable compositions of the invention which contain the amine-organoborane complex preferably displays thermal stability at, or above, room temperature. Thermal stability as used herein means the amine organoborane complex does not disassociate and initiate polymerization of the olefinic unsaturated compounds present in the composition. Thermal stability can be measured by determining the temperature at which the viscosity of the composition begins to increase. Preferably the temperature at which the viscosity of the composition increases is greater than about 40°C, more preferably greater than about 60°C and most preferably greater than about 80°C. The increase in viscosity indicates that the amine borane complex is disassociated and polymerization has been initiated. In the embodiment wherein the composition is used as an adhesive, the adhesive preferably demonstrates a lap shear strength of about 100 psi (689

kPa) or greater, more preferably about 250 psi (1724 kPa) or greater and more preferably about 400 psi (2758 kPa) or greater according to the following test procedure.

The adhesive components are mixed and applied to one or both substrates (1 in x 4 in x 1/8 in (25.4 mm x 101.6 mm x 3.2 mm) polypropylene coupons). Adhesive thickness is controlled by the addition of a few weight percent of glass beads between 0.005 to 0.030 inches in diameter (0.13 mm to 0.76 mm). The coupons are mated to provide 0.5 inch squared (161 mm^2) to 1.0 inch squared (645 mm^2) substrate overlap in a lap-shear testing configuration. The samples are held in place with metal binder clips to provide constant force and facilitate the elimination of air bubbles in the adhesive. The bonded samples were usually cured for at least about 24 hours before being mounted in a tensile testing apparatus fitted with a sample oven. The samples are evaluated at crosshead speeds of 0.05 (0.13 mm) and 0.5 (12.7 mm) inches per minute for room temperature and 110°C testing conditions, respectively. Maximum load (pounds) to break are recorded and maximum stress (psi) is calculated by dividing this load by the overlap area (inches squared).

Preferably the open time of the adhesive is about 3 minutes or greater, more preferably about 5 minutes or greater, and most preferably about 8 minutes or greater. Preferably the open time of the adhesive is about 30 minutes or less, more preferably about 25 minutes or less, and most preferably about 20 minutes or less. Open time as used herein is the time between initiation of polymerization and the time at which the adhesive can no longer be applied and used as an adhesive. If the open time is too long, poor bond strength is observed. If the open time is too short, the composition polymerizes before a link up with the substrate can be achieved.

Preferably the polymeric compositions of the invention have a suitable viscosity to allow application. Preferably the compositions have the viscosity of about 100 centipoise or greater, more preferable about 1,000 centipoise or greater and most about 20,000 centipoise or greater. Preferably the adhesive compositions have a viscosity of about 150,000 centipoise or less, more preferably about 100,000 centipoise or less and most preferably about 50,000 centipoise or less.

The following examples are included for illustrative purposes only and are not intended to limit the scope of the claims. Unless otherwise stated all parts and percentages are by weight.

Preparation Of The Organoborane/Amine Complex

50 cc of a 1M solution of organoborane, for example, tributyl borane (TBB) in ether solution (Aldrich), was added to a weighed round bottom flask. The solution was purged with nitrogen. A weighed amount of the amine, for example, pyrrolidine (4.97 g, 1:1.4 molar ratio of boron to amine), was added in small portions to the organoborane solution, maintaining the temperature below 40°C with an external ice bath. The amine was added to make a molar ratio of organoborane to amine of between 1:1 to a 1:3. The solution was stirred for about 30 minutes and then the solvent was removed on a rotary evaporator at less than 40°C. The weight of the flask and complex were periodically compared to the theoretical weight to assure that the solvent was completely removed. The complex was tested for pyrophoric reactivity by placing a drop on a paper towel and looking for charring of the towel. Some pyrophoric complexes can be made less or non-pyrophoric by adding additional amine (lowering the organoborane:amine molar ratio).

Preparation of Adhesive Compositions

Two component (part) adhesives were produced as described below. One component included the organoborane/amine complex (hardener) mixed with an acrylic resin, described below, and an antioxidant. The other component was the acrylic resin with an initiator, for example, acrylic acid, that decomplexes the boron/amine complex when mixed into the other component. The acrylic resin was a mixture of 250 g methylmethacrylate (MMA) and 80 g polymethylmethacrylate (PMMA, 350 K Mw). The MMA and PMMA were stirred or rotated overnight to mix the PMMA into the MMA. The resulting acrylic resin has a viscosity of about 25,000 centipoise (cP).

The first component (Part I) comprised 135 g acrylic resin, 6.6 g of a hardener, and 82.5 mg BHT. The second component comprised 135 g acrylic resin, 6.6 g acrylic acid (AA), 13.5 g fillers (glass beads, polypropylene ground flakes, etc.) (<10 percent), and 13.5 g tougheners (Stereon 840A block copolymer) (<10 percent)). The two

components of the adhesive composition were formulated to allow for a ratio of 1:1, 1:4, or 1:10 mixture of hardener:initiator, preferably 1:1.

The adhesive may be mixed in the desired ratio in air, in a bag, or through a pressurized gun. The adhesive was applied to a polypropylene test strip 1 inch (25.4 mm) wide with a ½ inch (12.7 mm) overlap and was tested for adhesive strength as described previously.

Thermal stability testing was performed according to the procedures provided below. The auto-initiation temperature was determined from the point at which the viscosity started to rise, indicating the onset of polymerization of the borane:amine containing resin without initiator. Onset occurred due to thermal destabilization of the boron/amine complex. Viscosity was measured continuously by a Brookfield viscometer (rotating cylinder at 50 rpm) as a function of a constant temperature ramp (about 1°C/min). The temperature at which the viscosity began to increase was noted and listed as the take off temperature.

In another method the time it took for the viscosity to reach 100 kcPs at ambient temperature (or elevated temperature) was determined by periodic measurement of the viscosity of a hardener and resin over a period of days. This was considered to be the useful lifetime of the resin.

Several complexes were prepared and tested in the composition as described herein. Table 1 contained the results of the testing.

The following abbreviations were used in Table 1.

TBB is tri-n-butyl borane.

DMAPA is dimethylaminopropylamine.

TiBB is triisobutylborane.

DEBM is diethylmethoxyborane.

DEBI is diethylisopropoxy borane.

TOB is tri-n-octylborane.

> means the substrate broke during measurement

Y means that paper ignited or charred when contacted with the borane:amine.

N means that paper did not ignite, char, smoke, or discolor when contacted by borane:amine.

Sl means that the paper showed slight evolution of smoke or discoloration, but not charring when contacted with borane:amine.

Table 1

Example	Borane	Amine	Molar B:Amine	Pyro-phoric ?	Take-off Temp (C)	Lap Shear (on PP) psi
1	TBB	Hexane diamine	1:1	N	44	>444
2	TBB	DMAPA	1:1.1	N	52	>900
3	TBB	DMAPA	1:1.2	N	53	>655
4	TiBB	DMAPA	1:1.25	N	39	>604
5	TBB	DMAPA	1:0.6	N	47	>929
6	TBB	Tetramethyl propane diamine	1:3	Y	46	192
7	TPB	DMAPA	1:1.1	N	>100	0
8	TBB	Aminopropyl morpholine	1:1.1	N	50	>682
9	TBB	Cyclohexylamine	1:1.2	sl	20	>933
10	TBB	Aminopropanol	1:1.2	N	20	>624
11	TBB	Morpholine	1:1.2	Y	20	>818
12	TBB	Ethanolamine	1:1.17	N	42	458
13	TBB	Piperidine	1:1.5	N	52	>783
14	TBB	Pyrrolidine	1:1.4	N	>100	679
15	DEBM	DMAPA	1:1.25	N	68	36
16	DEBI	DMAPA	1:1.25	N	77	64
17	TBB	Isophorone diamine	1:1.36	N	46	>422 >893
18	TBB	Methoxypropyl amine	1:1.36	N	63	>640
19	TBB	a-Methyl Benzylamine	1:1.6	sl	25	451
20	TOB	DMAPA	1:1.3	N	>100	471

Table 1 Continued

21	TBB	Aminopropyl propane diamine	1:1.2	N	64	>559
22	TBB	Aminoethoxy ethanol	1:1.3	N	25	>847
23	TOB	Methoxypropyl amine	1:1.3	N	68	110
24	TOB	Aminopropanol	1:1.3	N	53	79
25	TBB	Morpholine	1:3	N	42	>878
26	TBB	Aminopropanol	1:2	N	60	>419
27	TOB	Isophorone diamine	1:1.3	N	>100	0
28	TBB	Diisopropyl amine	1:2	Y	50	0
29	TBB	Cyclohexylamine	1:2	N	30	508
30	TBB	Piperidine	1:2	N	85	>775
31	TBB	Aminoethoxy ethanol	1:2	N	50	276
32	TBB	Pyrrolidine	1:1.4	N	>100	>709
33	TiBB	Pyrrolidine	1:1.4	N	>100	303
34	TBB	Piperazine	1:1.3	N	20	>749
35	TBB	Methyl pyrrolidinone	1:2	Y	20	0
36	TBB	Tetrahydro- thiophene	1:1.3	N	20	0
37	TBB	Diethanol amine	1:2	Y	65	61
38	TBB	Triethyl amine	1:2	Y	52	0
39	TBB	Dibutylamine	1:1.3	N	50	39
40	TBB	Dipropylamine	1:1.3	Y	52	0
41	TBB	Dioctylamine	1:1.3	N	58	192
42	TBB	Cyclopentyl amine	1:1.3	Y	25	>790
43	TBB	Cyclopentyl amine	1:2	N	25	>940
44	TiBB	Isophorone diamine	1:1.3	N	25	300
45	TOB	Methoxypropyl amine	1:1.3	N	50/83	
46	TBB	1,3,3 trimethyl 6-aza bicyclo [3,2,1] octane	1:1.3	N	25/>100	>426

Table 1 Continued

47	TBB	Dabco	1:1.3	sl	25	>774
48	TBB	Diamino maleonitrile	1:1.3	Y		NA
49	TBB	Thiazolidine	1:1.3	Y	25	>725
50	TBB	Thiazolidine	1:2	N	25	186
51	TBB	Urea	1:1.3	Y		NA
52	TBB	1,8 Diaza bicyclo[5,4] undec-7-ene	1:1.3	N	>100	>555
53	TBB	4-Dimethylamino pyridine	1:3	N	57	>581
54	TBB	Proline methyl ester	1:1.3	N		0
55	TBB	4-Bromo piperidine	1:1.3	Y		0
56	TBB	Acetaldehyde Ammonia Trimer	1:1.3	sl	67	0
57	TBB	1-Amino-4-Methyl Piperazine	1:1.3	N	25	145
58	TBB	Homopiperazine	1:1.3	N	25	638
59	TBB	2-Dimethyl-aminopyridine	1:3	sl	25	0
60	TBB	Pyridine	1:3	N	25	
61	TBB	Tetraaza adamantane	1:2	Y		0
62	TBB	Hexylamine	1:1.3	N	45	>885
63	TBB	Tetramethylguanidine	1:1.3	N	74	>616
64	TBB	Tetrahydropyrimidine	1:1.3	N	75	>736
65	TBB	2-Methyl 2-imidizole	1:1.3	N	35	>1000
66	TBB	3-Pyrroline	1:1.3	N	25	247

Table 1 Continued

67	TBB	Trimethylolpropane tris[poly(propylene-glycol), amine terminated]ether (avg mwt=432)	1:1.3	N	42	>620
68	TBB	Trimethylolpropane tris (2-methyl-1-aziridinepropionate	1:1.3	Y	<25	0

Binding Energies of Complexes

The organoborane/amine binding energies of several of the complexes were calculated using previously described computational methods. Comparison of results of amine/organoborane combinations listed in Table 1 with calculated binding energies in Table 2 revealed that binding energies less than about 10 kcal/mole were pyrophoric, and a high binding energy was correlated with higher thermal performance. Furthermore the calculated binding energy was correlated with the temperature at which the alkylborane-amine complex spontaneously disassociated. The disassociation temperature was easily determined by the so called "take-off" temperature provided in Table 1 at which time the polymerization proceeded in the absence of a de-complexing agent. The disassociation temperature may also be determined by differential scanning calorimetry. When applying differential scanning calorimetry, a sample of the complex was placed in a pan and the temperature of the pan was raised. At the same time a reference sample, usually an empty pan, was heated at the exact same rate and the difference in temperature between the sample and the reference was monitored and recorded using a differential amplifier. When reaction of the complex was observed an exotherm can be observed implying a release of heat due to insertion of oxygen into the alkyl-boron bond. No exotherm was observed when this experiment was performed under strictly inert conditions.

Table 2

Example	Lewis Acid	Amine	Binding Energy (kcal/mole)
2	TBB	DMAPA cyclic	20.4
2	TBB	DMAPA linear	15.9
25	TBB	morpholine	12.8
32	TBB	pyrrolidine	15.4
17	TBB	isophorone diamine cis	15.1
17	TBB	isophorone diamine trans	15.3
18	TBB	methoxypropylamine cyclic	20.1
18	TBB	methoxypropylamine, linear	15.4
21	TBB	aminopropylpropanediamine	18.3
38	TBB	triethylamine	0.0
47	TBB	Dabco	10.2
53	TBB	4-dimethylaminopyridine	16.2
60	TBB	pyridine	8.7
	TBB	dimethylaminoethylamine	18.8
	TBB	dimethylaminobutylamine	21.9
	TBB	propylamine	15.8

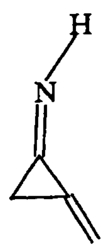
Table 2 Continued

	TBB	acetamidine	19.2
	TBB	guanidine	21.0
	TBB	cyclopropeneimine	17.0
	TBB	tetramethyldiaminocyclopropene imine	23
	TBB	3-N-methyl-3,4,5,6-tetrahydropyrimidine	16.4
	TBB	pyrazole	10.2
	TBB	3-aminopyrazole	13.1
	TBB	aziridine	18.0
	TBB	methylaziridine	14.9
	TBB	azetidine	17.9
	TBB	methylazetidine	12.2
	TBB	formaldimine	13.2
	TBB	benzaldimine	11.5
	TBB	3,4,5,6-tetrahydropyridine	12.2
	TBB	5,6-dihydropyridine	13.1
	TBB	cyclohexanone imine	12.8
	TBB	2-aminopropanol	15.8
	TBB	1,4-dihydropyrrole	15.0

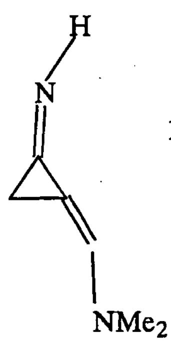
Table 2 Continued

	TBB	N-Methyl Tetrahydropyrimidine	16.4
	TBB	1-azabutadiene	13.8
	TBB	4-N,N-dimethylamino-1-azabutadiene	19.5
	TBB	4-Methoxy-1-azabutadiene	16.2
	TBB	4-Chloro-1-azabutadiene	11.0
	TBB	1-Azahexatriene	15.0

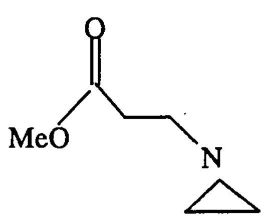
Among other compounds for which the binding energy is calculated, are those illustrated below with their calculated binding energies adjacent.



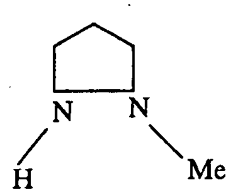
11.3



17.9



9.76



15.01

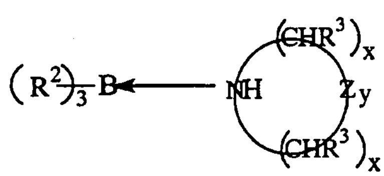
WHAT IS CLAIMED IS:

1. An organoborane/amine complex comprising an organoborane, comprising a trialkyl borane or an alkyl cycloalkyl borane and an amine selected from the group of amines having; an amidine structural component; aliphatic heterocycles having at least one nitrogen in the heterocyclic ring wherein the heterocyclic compound may also contain one or more nitrogen atoms, oxygen atoms, sulfur atoms, or double bonds in the heterocycle; primary amines which in addition have one or more hydrogen bond accepting groups wherein there are at least two carbon atoms between the primary amine and the hydrogen bond accepting group, such that due to inter- or intramolecular interactions within the complex the strength of the B-N bond is increased with the proviso that where the hydrogen acceptor group is an amine the amine is secondary or tertiary; and conjugated imines.

2. A complex according to Claim 1 wherein the complex of the organoborane and the primary amine corresponds to the formula

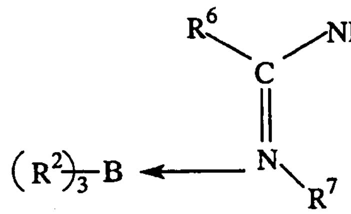
$$(R^2)_3B \longleftarrow NH_2(CH_2)_b(C(R^1)_2)_a- \quad ;$$

the organoborane heterocylic amine complex corresponds to the formula



;

the organoborane amidine complex corresponds to the formula



;

and

the organoborane conjugated imine complex corresponds to the formula

$$(R^2)_3B \leftarrow NR^7{=}CR^9{-}(CR^9{=}CR^9)_c \;;$$

wherein

B is boron;

R^1 is separately in each occurrence hydrogen, a C_{1-10} alkyl or C_{3-10} cycloalkyl;

R^2 is separately in each occurrence a C_{1-10} alkyl, C_{3-10} cycloalkyl or two or more of R^2 may combine to form a cycloaliphatic ring structure;

R^3 is separately in each occurrence hydrogen, a C_{1-10} alkyl or C_{3-10} cycloalkyl;

R^4 is separately in each occurrence hydrogen, C_{1-10} alkyl, C_{3-10} cycloalkyl, C_{6-10} aryl or alkaryl;

R^5 , R^6, and R^7 are separately in each occurrence hydrogen, C_{1-10} alkyl, C_{3-10} cycloalkyl, or two or more of R^5, R^6 and R^7 in any combination can combine to form a ring structure which can be a single ring or a multiple ring structure and the ring structure can include one or more of nitrogen, oxygen or unsaturation in the ring structure;

R^9 is independently in each occurrence hydrogen, C_{1-10} alkyl or C_{3-10} cycloalkyl, Y, $-(C(R^9)_2-(CR^9{=}CR^9)_c-Y$ or two or more of R^9 can combine to form a ring structure, or one or more of R^9 can form a ring structure with Y provided the ring structure is conjugated with respect to the double bond of the imine nitrogen;

X is a hydrogen-bond accepting group with the proviso that where the hydrogen bond accepting group is an amine it must be secondary or tertiary;

Y is independently in each occurrence hydrogen, $N(R^4)_2$, OR^4, $C(O)OR^4$, a halogen or an alkylene group which forms a cyclic ring with R^7 or R^9;

Z is separately in each occurrence oxygen or $-NR^4$;

a is separately in each occurrence an integer of from 1 to 10;

b is separately in each occurrence 0 or 1, with the proviso that the sum of a and b should be from 2 to 10;

c is separately in each occurrence an integer of from 1 to 10;

x is separately in each occurrence an integer of 1 to 10, with the proviso that the total of all occurrences of x is from 2 to 10; and

y is separately in each occurrence 0 or 1.

3. A complex according to Claim 2 comprising an aliphatic heterocylic amine wherein the amine is a five or six membered heterocylic compound.

4. A polymerizable composition comprising

a) a complex according to any one of Claims 1 to 3;

b) one or more of monomers, oligomers or polymers having olefinic unsaturation which is capable of polymerization by free radical polymerization; and

c) an effective amount of a compound which causes the complex to disassociate freeing the borane to initiate polymerization of the one or more monomers, oligomers or polymers having olefinic unsaturation;

wherein the compound which causes disassociation of the complex is kept separate from the complex until initiation of polymerization is desired.

5. A polymerizable composition according to Claim 4 wherein the one or more monomers, oligomers, and polymers have acrylate or methacrylate functionality.

6. A polymerizable composition according to Claims 4 or 5 wherein the compound which causes disassociation of the complex is an acid, aldehyde, isocyanate, acid chloride, or sulphonyl chloride, or a mixture thereof.

7. A method of polymerization comprising

a. contacting the components of the polymerizable composition of any one of Claims 4 to 6 under conditions such that the one or more monomers, oligomers, or polymers undergo polymerization.

8. A method of bonding two or more substrates together which comprises

a. contacting the components of the composition of any one of Claims 4 to 6 together under conditions such that polymerization is initiated;

b. contacting the adhesive composition with the two or more substrates;

c. positioning the two or more substrates such that the adhesive composition is located between the two or more substrates wherein they are in contact with one another; and

d. allowing the adhesive to cure so as to bind the two or more substrates together.

9. A method of modifying the surface of a low surface energy polymer by contacting a composition according to any one of Claims 4 to 6 with at least a portion of the surface of the low surface energy polymer and causing the complex to disassociate thereby initiating polymerization of the monomer, oligomers, polymers or mixture thereof such that the polymer formed is on the surface of the low surface energy polymer.

10. A method of coating a substrate which comprises contacting the components of the composition according to any one of Claims 4 to 6; contacting the contacted composition with one or more surfaces of a substrate; and curing the coating composition.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/33806

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08F4/52 C08F220/00 C08F265/06 B32B7/00 C07F5/02
C09D4/00 C09J4/06 C09J4/00 C09D4/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08F C09J B32B C07F C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 511 464 A (NAT STARCH CHEM INVEST) 4 November 1992 (1992-11-04) claims 1,9	1,2,4-8
X	US 5 539 070 A (ZHAROV JURY V ET AL) 23 July 1996 (1996-07-23) claims 1,3	1,2,4-9
X	LOVE, PETER ET AL: "Polar substituent effects in gas-phase Lewis acid-base equilibriums. I. Insrinsic basicity of amines" , J. AMER. CHEM. SOC. (1968), 90(10), 2455-62 XP000982168 tables I,EX.5 column 4 column 5	1,2

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
28 February 2001	14/03/2001

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Rose, E

5

INTERNATIONAL SEARCH REPORT

In ational Application No
PCT/US 00/33806

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE CHEMABS 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; FUJISAWA, SEIICHIRO ET AL: "Dental self - curing resins. XI. Characterization of several complexes of tri-n-butyl borane as an initiator" retrieved from STN Database accession no. 73:88532 XP002160417 abstract & IYO KIZAI KENKYUSHO HOKOKU, TOKYO IKA SHIKA DAIGAKU (1969), 3, 64-71 ,	1-10
A	US 5 935 711 A (DEVINY E JOHN ET AL) 10 August 1999 (1999-08-10) column 9, line 42-47	1-10
A	KOESTER, ROLAND ET AL: "Boron compounds. XXVII. Borylation of several amino carboxylic acids" , JUSTUS LIEBIGS ANN. CHEM. (1974), (1), 112-19 XP000982170 page 112-113	1-3

5

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Information on patent family members

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PCT/US 00/33806

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